

Preparation of novel magnetic polyurethane foam nanocomposites by using core-shell nanoparticles

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Abstract

Iron oxide magnetic nanoparticles (NP's) converted to the core-shell structures by reacting with *n*-(2-aminoethyl)-3-aminopropyl trimethoxysilane (AEAP) incorporated in polyurethane flexible (PUF) foam formulations. Fourier transform spectra, thermal gravimetric analysis, scanning electron images, thermo-mechanical analysis and magnetic properties of the prepared nanocomposites were studied. Obtained data shown that by the increasing of the amine modified magnetic iron oxide NP's up to 3% in the polymer matrix, thermal and magnetic properties improved in comparison with pristine foams. In addition, due to the presence of functional groups on the magnetic NP's surface, hard phases formation decrease in the bulk polymer and cause decreasing of glass transition temperature.

Keywords: *magnetic iron oxide, magnetic nanoparticles, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane (AEAP), Polyurethane flexible (PUF) foam.*

1. Introduction

Polyurethane's (PU's) as a well-known class of versatile polymeric materials prepare by a simple condensation reactions and because of their unique properties have been used in various applications namely, adhesives, coatings, elastomers and foams^[1,2]. In the foam categories, flexible families are the largest product family by quantity by having more than 40% of all PU foams production capacity. Flexible PU foam because of its lightness and strength is used as cushioning namely, car seats, mattresses and packaging, but having their main own merits and drawbacks^[3,4]. The main drawbacks refer to the low load bearing properties and low thermal stabilities in comparing to the other polymeric materials. In order to overcoming these drawbacks, in the recent years some novel nanocomposites are prepared^[5]. Nanocomposites display prior properties when compared with their microcomposites counterparts, due to the much stronger interactions between the dispersed nanoparticles (NP's) domains and the polymer matrix^[6]. In this case and in flexible PU foams, the incorporation of nanoparticles increase foam density as well as improve compression and tear properties^[7]. Literature survey reveals the application of well-known NPs in the flexible foam formulations namely, fumed silica^[8], calcium carbonate^[7], nanofibers^[9], carbon nanotubes^[9,10], zinc borate, phosphorous and expandable graphite^[11] in order to improving of thermal, mechanical, acoustic and flame retardancy properties, respectively because of the high performances of nanoparticles in improving of target properties^[12]. Above all, the roles of inorganic such as magnetic iron oxide NP's (MNP's) by having unique and high performances are undeniable. For example, application of MNP's in the polymer matrix leads to the improvements in the thermal and magnetic properties and open new windows for the preparation of the new magnetic materials namely, magnetic polyurethane foams^[13]. Among all of merits, the surface energy of MNP's is very high and tends to agglomerate and is very difficult dispersed uniformly in to the polymer matrix^[14]. Surface modification of MNP's is used to improve the performance of nanoparticles and create

a good linkage between inorganic filler and organic polymer matrices^[15]. In this case, coupling agents has been used for modification of magnetic iron oxide via non-magnetic shell formation of silica what can reduce the agglomerating, enhances thermal resistance of iron oxide nanoparticles and improve the compatibility between magnetic Fe₃O₄ NP's and PU matrices^[16,17].

Magnetic nanoparticles incorporated in to the polymer matrix by some methods, such as melting, solution and in-situ polymerization which the later is the most common and well known method. The in-situ polymerization of MNP's in the polymer matrix is an excellent method to control the mean size and size dispersion of a nanoparticle population, which are crucial factor in determination the properties of the nanocomposites^[18]. In our previous work, magnetic polyurethane rigid foam nanocomposite were prepared by incorporation of Fe₃O₄@SiO₂ NP's in polymer matrix. The results indicate the performance of MNP's in enhancing of the thermal resistances, storage modulus, and magnetic properties of filled rigid foam in comparison with pure PU^[5].

In this study, the super paramagnetic Fe₃O₄@AEAP NP's incorporated in to the PU flexible foam. In order to improve the dispersion of Fe₃O₄ NP's in PU matrix and compatibility between Fe₃O₄ NP's and PU matrix, NP's were modified with AEAP and Fe₃O₄@AEAP-PU flexible foam nanocomposites were prepared via in-situ polymerization. Our data showed superior and significant thermal stability and magnetic properties of resultant foams when MNP's incorporated up to 3.0%.

2. Experimental

2.1 Materials

Daltoflex EC[®] 20240 formulated virgin polyol. The polyol (propylene oxide-ethylene oxide copolyether) as a colorless viscous liquid, having viscosity 1.250 Pa s at 208 °C, specific gravity 1.035 g/cm³ at 208 °C, fire point 240 °C, Mw 1900,

functionality 2 and hydroxyl numbers 59 mg KOH/g. Isocyanate was Suprasec 2027 diphenylmethanediisocyanate (MDI)-based prepolymer (dark brown liquid, having viscosity 0.220 Pa s at 258 °C, specific gravity 1.23 g/cm³ at 258 °C, NCO value 30.9% by weight of NCO groups analysis (group weight: 42 g/mol), average functionality 2.7, flash point 233 °C, and fire point 2458C). Daltoflex EC 20240 and Suprasec® 2027 are chlorofluorocarbon (CFC) free systems, purchased from Huntsman Company with starting formulation as Daltoflex EC 20240: 100 pbw and Suprasec 2027: 65 pbw.

The following reagents were purchased from Merck and used as received without further purification: Iron (II) chloride tetrahydrate (FeCl₂·4H₂O, 99.7%), iron (III) chloride hexahydrate (FeCl₃·6H₂O, 99.0%), ammonia (NH₃·H₂O, 25%-28%), ethanol (C₂H₅OH 99.7%), n-(2-aminoethyl)-3-aminopropyl trimethoxysilane (AEAP) and citric acid.

2.2 Instruments

Morphology studies and particle size of magnetic nanoparticles (Fe₃O₄) were done on a field emission scanning electron microscopy (Hitachi model Se 4160). Fourier transform infrared spectroscopy (FT-IR) spectra were done on a Bruker Tensor 27 spectrophotometer. The thermogravimetric analysis (TGA) of Fe₃O₄ and Fe₃O₄@AEAP NP's and magnetic nanocomposite were performed on a Perkin-Elmer Paris Diamond TG/DTG under N₂ and O₂ atmosphere at a heating rate of 10 °C/min. Thermal mechanical analysis (TMA) was carried out by using a Linseis TMA instrument (TP 1000, Germany) over a temperature range from -100 to 250 °C and in compression mode. Magnetic hysteresis loops of magnetic foams were measured *via* a vibration sample magnetometer (VSM). To disperse modified magnetic nanoparticles in the polymer matrix, an ultrasonic homogenizer (Hielscher, Up 200S, Germany) was used.

2.3 Synthesis of Fe₃O₄@AEAP nanoparticles

The magnetic NP's were prepared through a co-precipitation method by the reaction of ferric and ferrous (2/1 in mol/mol) in ammonia solution as reported by elsewhere^[5]. Fe₃O₄@AEAP NP's was synthesized in two steps which in the first step, magnetic NP's (100mg) was dispersed in ethanol/water (5/1) (110 ml) and sonicated for 20 min by drop wise addition of acetic acid and adjusting of pH at 4. Then AEAP (0.3 ml) was added to the solution and the mixture was stirred mechanically at room temperature for an additional 2 h. Finally, the core-shell NP was separated and washed with distilled water (2× 100 ml), collected and dried at 50 °C in an oven overnight and characterized.

2.4 Synthesis of polymer

2.4.1 Foam processing

When the isocyanate is mixed with the polyol, the exothermic chemical reactions start. The foam processing is followed by the cream time, gel time, rise time and tack-free time^[15]. The cream time is the first step and corresponds to the start of bubble rise and the time at which the clear

mixture turns creamy and starts to expand. Gel time is the first point of stable network formation by intensive allophanate cross-links as well as urethane. Rise time is the time between the start of the final mixing and the time of complete expansion of the foaming mass. At the tack-free time, the outer surface of the foam loses its adhesiveness and the foam can be removed from the mold.

2.4.2 Synthesis of Fe₃O₄@AEAP-PU flexible foam nanocomposite

In the first step, modified MNP was dispersed in the polyol matrix in weight percents of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 by vigorous stirring for 3min and the pre-mixture was sonicated for 4 min *via* an ultrasonic probe to the formation of a homogeneous mixture. In the next step, nano-particulated polyol was hand mixed with MDI in a 250 ml paper cup at 10:6 (polyol/MDI) weight ratios. Finally the sample was kept at room temperature for 24h for complete post curing and further testing^[5]. The reaction pathway of PU-flexible foam nanocomposite formation is shown in Scheme 1. As shown in scheme, by incorporation of AEAP modified magnetic nanoparticles in polyurethane matrix, the interaction between isocyanate group and amino-group with formation of urea fragments have been created.

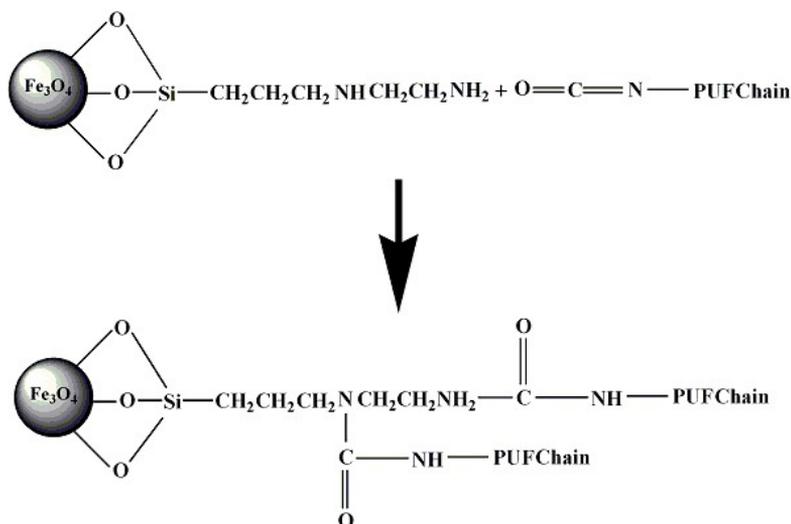
3. Result and Discussion

3.1 Characterizations of magnetic and Fe₃O₄@AEAP nanoparticles (FT-IR, TGA and SEM analysis)

The AEAP coating on the Fe₃O₄ NP's was confirmed by FT-IR spectroscopy (Figure 1). The stretching vibration frequencies at 480 and 582 *Cm*⁻¹ are attributed to the Fe-O functional groups of magnetic nanoparticles. After the coating of AEAP to Fe₃O₄ NP's, the Fe-O-Si band stretching vibration appeared at 584 *Cm*⁻¹ and overlaps with Fe-O bands^[19]. In addition, the bands at 1091 *Cm*⁻¹ corresponded to the stretching vibration of the Si-O bond. The absorption band at 3479 *Cm*⁻¹ in the spectrum of the Fe₃O₄@AEAP NP is attributed to the -NH group introduced from the AEAP. Furthermore, the presence of band at 2896 and 2972 *Cm*⁻¹ are corresponded to the stretching vibration of C-H groups on AEAP^[6,20]. The obtained results from FTIR studies resulted that the surface of the Fe₃O₄ NP's was successfully modified with AEAP.

Another method for confirmation of surface modification is thermo-gravimetric analysis method. Figure 2 shows the TGA of pure MNP's (Fe₃O₄) and Fe₃O₄@AEAP NP's. The weight loss of pure MNP's take place below 120 °C and calculated as 5% which attributed to the evaporation of water molecules^[21]. In addition, at 700 °C the total weight losses of Fe₃O₄@AEAP NP are assigned as 22%. Taking in to account the weight loss of pure MNP's, it could be expected that the content of AEAP moiety on the magnetic NP's surface was about 17%.

For morphology studies of Fe₃O₄@AEAP NP, SEM images has been used and data shown in Figure 3. It can be observed from the images that magnetic and Fe₃O₄@AEAP particulates have uniform spherical shapes with the size in the range of 30-40 nm and 50-60 nm, respectively.



Scheme 1. The formation of PU flexible foam nanocomposites.

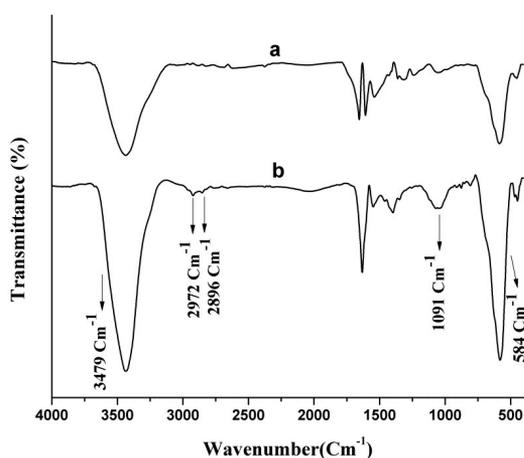


Figure 1. FT-IR spectra of (a) Fe_3O_4 and (b) $\text{Fe}_3\text{O}_4\text{@AEAP}$ nanoparticles.

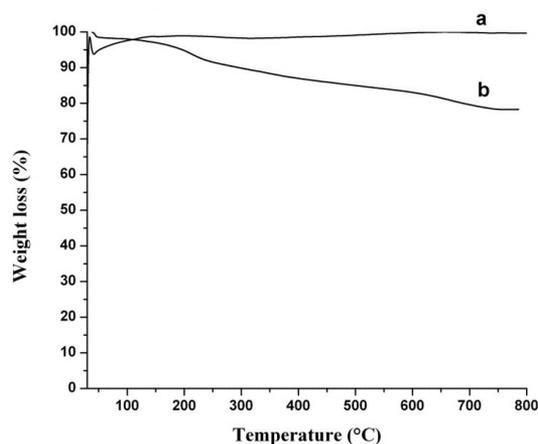


Figure 2. TGA curves for (a) Fe_3O_4 and (b) $\text{Fe}_3\text{O}_4\text{@AEAP}$ nanoparticles.

3.2 Characterization of PU-flexible foams nanocomposite

3.2.1 FT-IR analysis

The ATR spectra of $\text{Fe}_3\text{O}_4\text{@AEAP/PUF}$ nanocomposite containing $\text{Fe}_3\text{O}_4\text{@AEAP}$ NP's (1.5 to 3.0%) are shown in the Figure 4. As shown in the spectra, the absorption at 1105 Cm^{-1} is related to $-\text{C}-\text{O}$ functional group. Similarly, band at 1234 Cm^{-1} corresponded to the C-N functional groups (FG) of the urethane. Furthermore, it can be seen that all PU samples have similar vibration bond at 3348 Cm^{-1} (hydrogen-bonded stretching vibration of urethane groups), 1595 Cm^{-1} (N-H bending vibrations), and 1714 Cm^{-1} (C=O) what are corresponded to the urethane functional groups. In the meantime and as shown in figure, the $-\text{NCO}$ groups appeared at 2293 Cm^{-1} and indicated that the isocyanate

groups have not completely reacted^[22]. Finally, the bands at 2889 and 2976 Cm^{-1} are assigned to the asymmetrical C-H stretching and symmetrical stretching of polyether groups in the aliphatic chains, respectively^[23,24].

3.2.2 Morphology studies (SEM)

Surface morphological analysis of the magnetic nanocomposite was done by scanning electron microscopy (SEM) and shown in Figure 5 and cell density (N_f) is calculated by using Equation 1^[12]. In this equation, n is the number of cells, A the area of the micrograph in Cm^2 , and M is the magnification factor. As shown in the Table 1, by increasing of modified MNP's from 1.5 to 3%, cell density was increased and cell size was reduced. These results indicate that the nature of the dispersion plays a fundamental role in controlling the cell size during foaming.

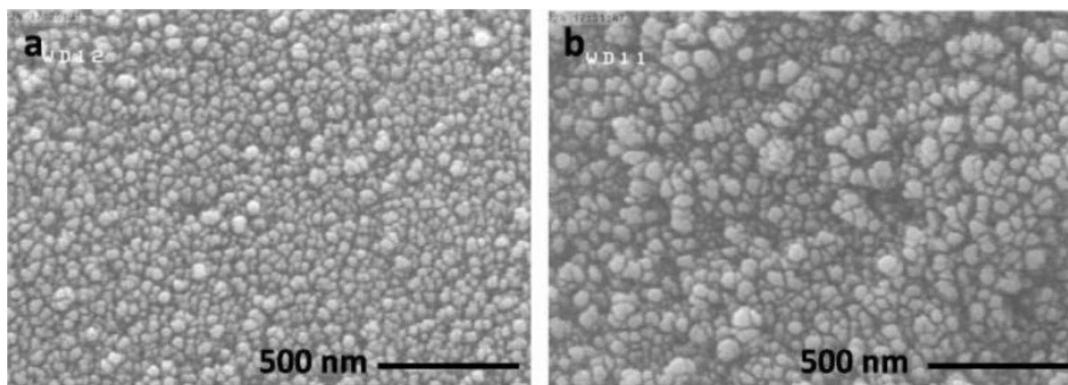


Figure 3. FE-SEM images of synthesized (a) Fe₃O₄ and (b) Fe₃O₄@AEAP nanoparticles.

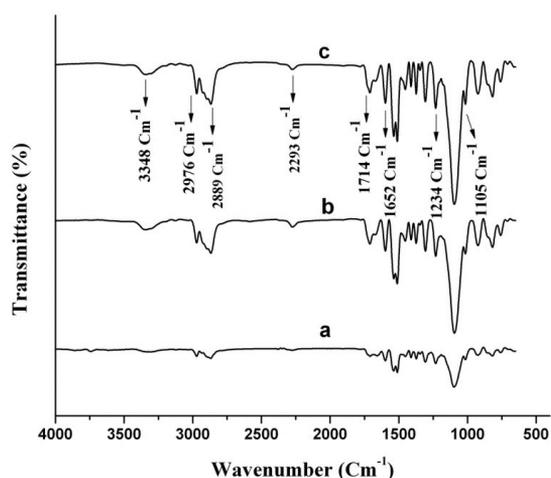


Figure 4. IR-ATR spectra of Fe₃O₄@AEAP-PUF foams, with different content of Fe₃O₄@AEAP: (a) 0; (b) 1.5 and (c) 3.0%.

Table 1. Cell densities of PUF foams.

NP's (%)	a(0.0)	b(1.5)	c(3.0)
N _f (Cells/Cm ³)×10 ⁵	0.198	0.298	0.364

$$N_f = \left(\frac{nM^2}{A} \right)^{\frac{3}{2}} \quad (1)$$

In addition, the foam density (D) is calculated using the Equation 2:

$$D = \frac{M}{V} \quad (2)$$

In this equation, M is mass (gr) and V is the volume (Cm³) of the foam, respectively. As shown in Table 2, by increasing of the nanoparticles content, the foam density is increased. In the other words, foam densities is controlled by the competitive process between the cell nucleation, its growth, and coalescence and reveal that the nucleation process occurred in the well-dispersed modified MNP's in the polymer matrix. In addition, MNP's act as nucleation site

to aid the bubble nucleation process during cell formation and enhances the cell densities.

3.2.3 Thermo-gravimetric analysis (TGA)

In order to evaluate the role of MNP's on thermal properties of PUF's, TGA experiments were done on nanocomposite samples and data compared with pristine one data. As shown in Figure 6 and Table 3, by incorporation of Fe₃O₄@AEAP NP's from 0.5 to 3.0%, the performed thermal stability was observed for 3% filled sample. This behavior can be interpreted that, MNP's have high specific thermal capacity that caused to heat preservation, acts as a thermal insulator, delay the degradation process and reduces the heat conduction to the PU matrix.

3.2.4 Magnetic properties analysis (VSM)

Figure 7, presented the magnetic hysteresis loops of the Fe₃O₄@AEAP-PU flexible foams nanocomposite with different content of Fe₃O₄@AEAP NP's. From magnetic hysteresis loops, when the content of MNP's varied from 1.5 to 3.0%, the saturation magnetization (M_s) is raised from 0.52 to 0.64 emu/g, respectively which indicate nanocomposite reveals super paramagnetic behavior, because no remanence magnetization is observed. Furthermore, magnetic nanocomposite could be magnetized and modulated via an external magnetic field.

3.2.5 Thermo-mechanical analysis (TMA)

Linear thermal expansion coefficient (α) and glass transition temperature (T_g) are two important measurements in the thermal analysis of the polymers and expected by TMA results. In this study, α is calculated according to Equation 3, where dL is length changes, dT is temperature changes and L₀ is initial length of the sample. Thermo-mechanical behaviors of the nanocomposite samples are shown in the Figure 8. As shown in Figure 8 and 9, by incorporation of modified MNP's from 1.5 to 3.0% in PU matrix, the T_g value was decreased in comparison with pure foam. Additional, reduction of T_g in modified MNP's samples affected by some factors, such as low cross link density, restriction of hard phase domain and enhance in chain mobility.

$$\alpha = \frac{dL}{dT \times L_0} \quad (3)$$

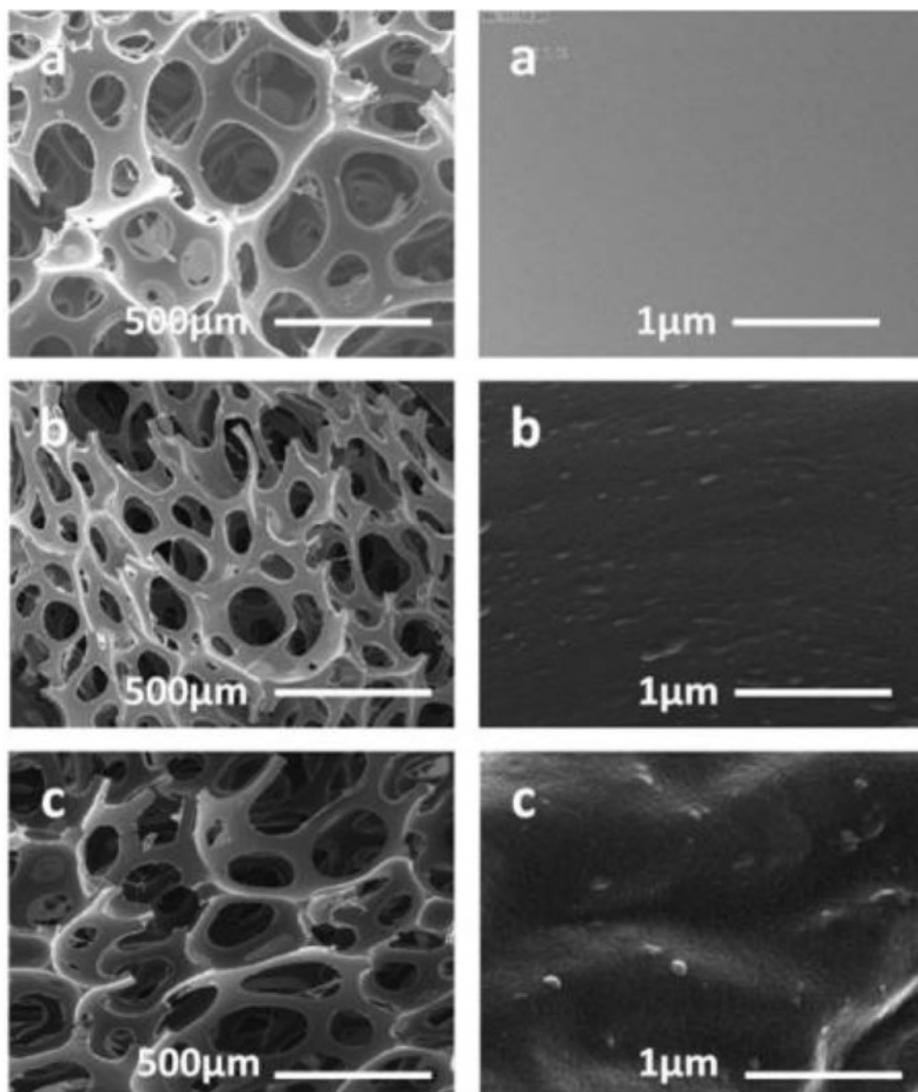


Figure 5. FE-SEM images of PUF foams nanocomposite with different contents of $\text{Fe}_3\text{O}_4@AEAP$: (a) 0.0; (b) 1.5 and (c) 3.0%.

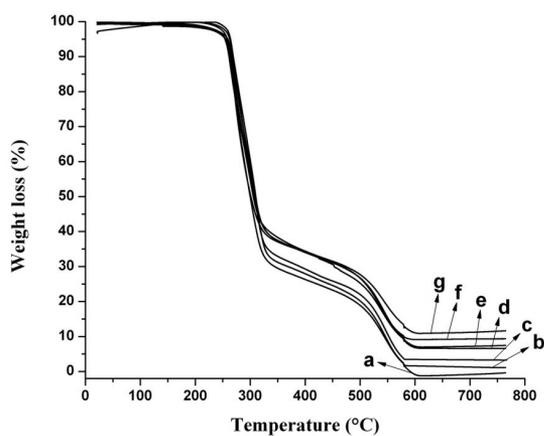


Figure 6. TGA curves of PUF foam nanocomposites with different contents of $\text{Fe}_3\text{O}_4@AEAP$ nanoparticles: (a) 0.0; (b) 0.5; (c) 1.0; (d) 1.5; (e) 2.0; (f) 2.5 and (g) 3.0%.

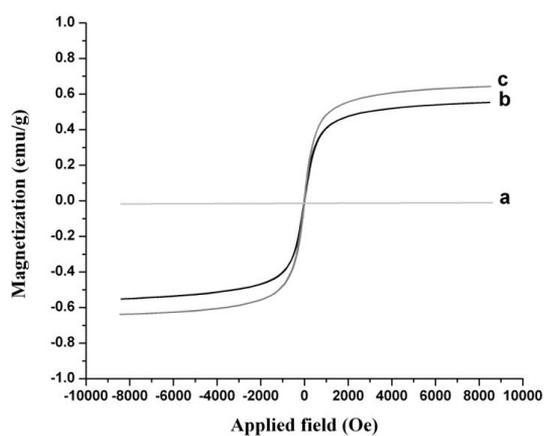


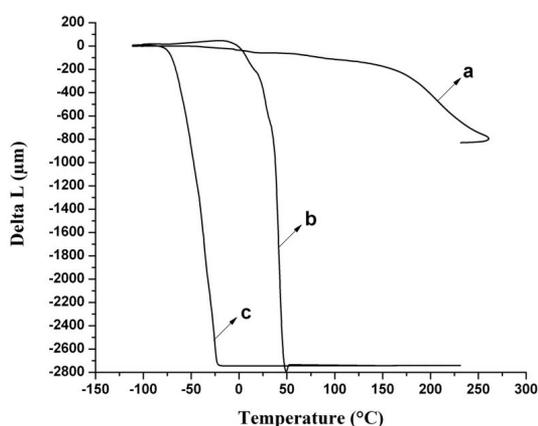
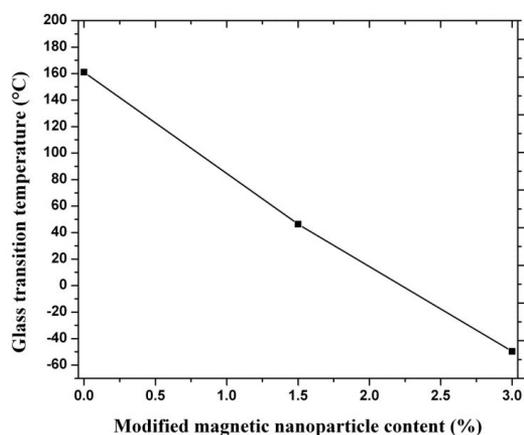
Figure 7. Magnetization hysteresis loops of $\text{Fe}_3\text{O}_4@AEAP$ -PUF foams with different content of $\text{Fe}_3\text{O}_4@AEAP$ nanoparticles: (a) 0.0; (b) 1.5 and (c) 3.0%.

Table 2. Foam densities of prepared PUF foams.

Samples (%)	a(0.0)	b(0.5)	c(1.0)	d(1.5)	e(2.0)	f(2.5)	g(3.0)
Density (g/cm ³)	0.027	0.038	0.042	0.047	0.052	0.055	0.058

Table 3. T_{5%}, T_{10%}, T_{max} and ash content (%).

Fe ₃ O ₄ @AEAP (%)	T _{5%} (°C)	T _{10%} (°C)	T _{max} (°C)	Ash content (%)
a (0.0)	258.01	265.54	765.02	0.14
b (0.5)	259.66	268.01	764.80	1.11
c (1.0)	262.57	268.73	767.60	3.31
d (1.5)	263.12	270.05	765.25	6.59
e (2.0)	261.93	270.90	764.88	7.46
f (2.5)	264.36	271.27	766.76	9.35
g (3.0)	265.70	272.70	767.75	11.63

**Figure 8.** TMA curves of PUF foam nanocomposites with different contents of Fe₃O₄@AEAP: (a) 0.0; (b) 1.5 and (c) 3.0%.**Figure 9.** Glass transition temperature (T_g) of PUF foam nanocomposite with different percent of MNP's (0.0, 1.5 and 3.0).

4. Conclusion

In summary, magnetic polyurethane flexible foam nanocomposites are prepared by incorporation of synthesized Fe₃O₄@AEAP NP's in polymer matrix via in-situ polymerization. The presence of reactive functional

groups on MNP's surface improved the interaction between inorganic nanofiller and polymer matrix. The results of the thermo-gravimetric analysis showed thermal stability of MNP's nanocomposite enhanced because of MNP's act as a thermal barrier. TMA results T_g decrements due to reduction of hard phases domain and limitation of soft segment mobility and freedom. The FE-SEM images showed that the modified MNP's acted as the nucleation sites during cell formulation and led to the cell size decrements as well as cell density increments. Finally VSM results indicated super paramagnetic behavior for nanocomposites.

5. Acknowledgements

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